Measuring pH Correctly

Pharma Conference
GEP-Good Electrochemistry Practice

November, 18 - Cairo

METTLER TOLEDO
Agenda

- Introduction
  - Sensor
  - Sample
  - FAQ Examples
Good practice needed for consistent accurate results

= Widely used technique and appears to be straight forward…..

But: many possibilities for errors in the whole system
- Meter
- Environment
- People
- Documentation
- Electrode
- Sample

→ Only correct usage and maintenance of the system guarantees reliable results
**Installation and qualification are crucial**

Due to time reasons only shortly discussed here

- Necessary to make sure that the systems works according to manufacturer’s specifications at your site
  - and is suitable for your purpose
  - which is proven with suitable documentation
Calibration of sensor inputs

Once to twice annually as part of operational qualification

- In case of problems: first make sure meter is not the cause
- Sometimes the meter or electrode cable has a short
  - No signal due to working electrode
  - Ease to verify (other cable, resistors)
- Get certificates for prove
- Calibration service can be included in service contracts
Environment

- During installation qualification, **the suitability of the environment must be verified**
  - Appropriate temperature
  - Minimal temperature fluctuations
  - Humidity appropriate
  - Avoid strong air flow close to the meter
  - Have enough space to work (accidents)
Introduction

Training

- The more you aware of possible risks, the better you can minimize them
- Ensures correct handling of the system
- Saves time troubleshooting
- Helps understanding possibilities and limits of the measuring system

Documentation

- If is not documented, it is not done
- Ensures traceability
- Supports legal requirements
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Sensor

Daily tasks

- Electrode preparation
- Electrode storage
- Electrode cleaning
- Electrode calibration

To get

- Longer lifetime (saves money)
- Constantly reliable results
- Fewer problems (saves time)
Electrode lifetime

The pH sensitivity of the gel layer **sinks with age**

**The aging process is temperature dependent**

Example lifetimes at different temperatures (same usage) assuming:

Application of good practices with measurement in aqueous solutions and pH range 1 to 12

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Approximate Lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Room temperature</td>
<td>1 to 3 years</td>
</tr>
<tr>
<td>90°C</td>
<td>3 to 9 months</td>
</tr>
<tr>
<td>120°C</td>
<td>6 to 12 weeks</td>
</tr>
</tbody>
</table>
Electrode lifetime

- Electrodes don’t last forever and **have to be replaced sometimes**
- Aging depends also on handling, sample, frequency of usage
- Indication of too old electrode

  - X slower response times
  - X higher membrane resistance
  - X smaller slope
  - X bigger offset
Sensor

Electrode preparation – reference electrolyte

Replace reference electrolyte regularly (e.g. once per months)

✓ Less crystallization at the diaphragm
✓ Less impurities in the electrolyte
✓ Constant high ion concentration

! Don't fill up, empty it completely
✓ Fill it again using fresh electrolyte

Electrolyte level in electrode must be higher than the sample
✓ Avoid the reflux of sample into the electrode (contaminations)

No air bubbles behind junction
✓ Vertical shaking of electrode to get rid of them
Electrode preparation – dry membrane

Cause
- Measuring in non-aqueous or ion deficient media
- Wrong storage

Effect
- Reduced sensitivity of glass (gel layer “washed out”)
- Unstable signal

Action
- Conditioning in 0.1 mol/L HCl during 12 hours
Electrode preparation – out-of-specs

Cause
- Age in general
- Usage for samples which attack the glass

Effect
- Offset too big and slope too low
- Unstable signal and sluggish response

Action
- Reactivation of membrane: place electrode in reactivation solution (NH₄HF₂) for 1-2 minutes

OR.... Replace the electrode!
Electrode storage

Objective

- Ensure that the pH sensitive gel layer which forms on the pH glass membrane remains hydrated and ion rich

Always store

- In inner electrolyte (e.g. 3 mol/L KCl)
- In buffer solutions (e.g. pH 4 or 7)
- In HCl diluted (approx. 0.1 mol/L)
- Together with sample (same conditions)

Never store

Dry, in distilled water or non-aqueous solutions

→ Reduces lifetime

✓ Needs conditioning before use (costs time)
Sensor

Electrode cleaning

Aqueous sample
✓ Rinse with distilled water after every measurement (contamination of next sample)
✓ Dip it dry with paper towel
! Never wipe it with paper towel (electrostatics)

Non-aqueous or dirty sample
✓ First rinse with solvent to get rid of dirt which is not water soluble
✓ Rinse with distilled water, dip it dry
✓ Condition in aqueous solution
Electrode cleaning - diaphragm

Blocked with silver chloride (AgCl)
✓ With concentrated ammonia

Blocked with silver sulfide (Ag₂S)
✓ With 8 % thiourea in 0.1 molar HCl

Blocked with proteins
✓ With 5 % pepsin in 0.1 molar HCl

Other junction blockages
✓ In ultrasonic bath with water or 0.1 molar HCl

Treat one hour, rinse with distilled water, and perform a new electrode adjustment
Sensor

Electrode calibration

Possible errors
- Not done frequently enough
- Done at a different temperature than subsequent measurement
- Wrong or contaminated buffers used

Actions
- Calibrate at least once per day, more if high temperature fluctuations
- Make sure conditions at calibration and measurement (temperature, stirring etc.) are equal
- Always use fresh buffers – if buffers not accurate, pH calibration is not accurate and the measurement will not be accurate
- Perform at least a two point calibration
- Make sure the calibration points frame the expected sample pH
Electrode calibration – buffer handling

- Buffers have expiry date – don’t order in bulk
- Store well sealed at room temperature
- Take out needed amount and close bottle immediately again
- Never calibrate electrode directly in the bottle
- Never re-use already used buffer solution
- Take single-use buffer sachets

Buffers are “testing equipment”!
Electrode calibration – indicating electrode condition

- "Offset" value (mV) – indicates the age of electrode and provides an estimation when the electrode need to be changed.
- Calibration Slope (%) – indicates the sensitivity of the glass membrane

- Recommended offset range at pH 7.00 is ± 30mV.
- Recommended calibration slope range is 95% - 105%.

(DIN 19263 requirements: Offset 0 ± 30 mV; Zero Point: pH₀ = 7 ± 0.5 pH)

Electrode condition

- slope: 95-105 %
  offset: ± (0-15) mV
  Electrode is in good condition

- slope: 90-94 %
  offset: ± (15-35) mV
  Electrode needs cleaning

- slope: 85-89 %
  offset: ± (>35) mV
  Electrode is faulty
In brief

If electrode is not performing well

- Membrane dehydrated, contaminated or damaged
- Electrolyte contaminated, has crystallized, hasn’t been filled enough or is missing, has too low ion concentration
- Air bubbles behind the ceramic junction
- Diaphragm (junction) contaminated or blocked
- Electrode worn out (out of specs), is too old
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Temperature errors

!!! Change of pH value of sample with temperature

! Change of electrode slope with temperature
! Isothermal intersection differs from theoretical value
pH value of a solution differs **with temperature (!)**

<table>
<thead>
<tr>
<th>Samples</th>
<th>20°C</th>
<th>30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl 0.001 mol/L</td>
<td>pH 3.00</td>
<td>pH 3.00</td>
</tr>
<tr>
<td>NaOH 0.001 mol/L</td>
<td>pH 11.17</td>
<td>pH 10.83</td>
</tr>
<tr>
<td>Phosphate buffer</td>
<td>pH 7.43</td>
<td>pH 7.40</td>
</tr>
<tr>
<td>TRIS buffer</td>
<td>pH 7.84</td>
<td>pH 7.56</td>
</tr>
</tbody>
</table>

* Each solution has **its own temperature dependence!**

* It is NOT possible to compensate for this effect with a pH meter (only pH values measured at the same temperature can be compared)

* Exception: temperature dependence of standard buffers is well known

* Modern pH meters have tables integrated to automatically compensate for this effect during calibration – doesn’t help for sample measurement
Electrode slope changes with temperature

<table>
<thead>
<tr>
<th>°C</th>
<th>s (mV/pH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>-56.2</td>
</tr>
<tr>
<td>20</td>
<td>-58.2</td>
</tr>
<tr>
<td>25</td>
<td>-59.2</td>
</tr>
<tr>
<td>30</td>
<td>-60.1</td>
</tr>
<tr>
<td>40</td>
<td>-62.1</td>
</tr>
<tr>
<td>50</td>
<td>-64.1</td>
</tr>
</tbody>
</table>

- Nernst's law: slope $s = - \frac{2.3 \cdot R \cdot T}{F}$ is temperature dependent
- Accurate and precise pH meas. mean accurate and precise Temp. meas.
- Modern pH meters are operated with a temperature probe connected
- They automatically correct for this effect during calibration and sample measurement by using the correct slope for the temperature
Stirring

- DIN19268 requires stirring

! Lowered reproducibilities when stirring during measurement

! Signal not stable due to instable diffusion conditions at the diaphragm when stirring

**Practical approach**

- Fist stir to equilibrate and homogenize it
- Then switch off the stirrer and measure
- Or just stir gently
- Use the same way for both calib. and meas.
Sample

Further sample effects

X Sample stored incorrectly (decomposition, alterations)
X Sample not homogeneous

Measure the sample, not your sensor.
With very small samples, the sensor can take so long to reach equilibrium that the sensor temperature is wrongly interpreted as the sample temperature. The sample mass is negligible compared with the sensor mass, so take the time necessary to ensure that you actually measure the sample temperature.
Summary

Simply the wrong way

X Filling hole closed during measurement
X Storage in deionized water
X Wipe to clean glass membrane
X Calibration once a week
X Temperature has no influence
X Never replace electrolyte
X Re-use buffers for calibration
X Stir extremely fast during measurement
and …

pH measurement can’t go wrong !!!! X
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FAQ Example 1

How often do I need to calibrate my pH electrode?

It depends on the type of sample, the electrode and the required accuracy

For accurate measurements, **at least daily**

- Dirty and non-aqueous samples need more frequent calibrations
- Old electrodes need more frequent calibrations
- Always after changing electrode or after long storage, after replacement of electrolyte, after cleaning of blocked diaphragm, after rehydration of electrode, after regeneration of electrode
FAQ Example 2

How many times can I use my pH buffers?

Only once!

Always use fresh buffers

Buffers are your calibration tools and need to be treated as such

Buffers have an expiry date
FAQ Example 3

Why does it take 3 minutes or more to get a result?...

This is not normal!

- Wrong electrode selected (select correct one)
- Electrode is too old (regenerate or buy new one)
- Not enough electrolyte or electrolyte is diluted or contaminated (empty old electrolyte and fill up with fresh electrolyte)
- Electrode is dry (rehydrate)
- Sample is not homogenous (homogenize, stir)
- Settings for auto endpoint on meter too strict for application (change)
- Continuous temperature fluctuations (change)
Questions?

Please visit our dedicated pH website
WWW.electrodes.net